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ISOMERIZATION OF 1-BROMOPENTABORANE(9)
BY BASE CATALYSIS ¹

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Sir:

The reversible conversion of 1-BrB₅H₈ ² to the previously

(2) T. Onak and G. B. Dunks, Inorg. Chem., 3, 1060 (1964) and earlier references there cited.

unknown and far more volatile isomer 2-BrB₅H₈ is catalyzed by hexamethylenetetramine. Also effective is dimethyl ether, but with side reactions qualitatively varying with temperature; one result is a new synthesis of 1-CH₃B₅H₈.

The relatively low volatility of 1-BrB₅H₈ would relate to the negative charge at the apex of the B₅H₉ skeleton; ³ and

(3) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York, N. Y., 1963, p. 110.

and the enhanced B-Br bond polarity would gain effect from a probable molecular packing with the apex bromine atom near to the four basal boron atoms of another molecule. Such packing would be inconvenient for 2-BrB₅H₈. The CH₃B₅H₈ isomers show a smaller and opposite difference of volatility.

Syntheses. Direct Al₂Cl₆-catalyzed bromination of B₅H₉ gave exclusively 1-BrB₅H₈, ² but one experiment without any catalyst (12 hr., warming to 25°) gave a 4% fraction later recognized as 2-BrB₅H₈, with an 82% yield of 1-BrB₅H₈.

Isomerization. Freshly vacuum-sublimed (CH₂)₆N₄ (ca.

100 mg.) and 0.936 mmole of 1-BrB₅H₈ (20 hr., sealed tube, 35°) gave 0.461 mmole of 1-BrB₅H₈ and 0.454 mmole of far more volatile material having the same molecular weight (143.0 vs. 142.05 calcd.). Hydrolytic analysis of this gave 1.007Br⁻, 5.024B(OH)₃, and 10.80H₂ per molecule. These results (and the absence of side reactions) prove the isomer.

Reversal of the isomerization was demonstrated by exposing 78 mg. of pure 2-BrB₅H₈ to (CH₂)₆N₄ (18 hr., 24°). The yield of 1-BrB₅H₈ was 12 mg. (15%) and the recovery of 2-BrB₅H₈ was 65 mg. (83%).

Physical Properties. As indicated by the data of Tables I and II, the isomers could be separated easily by high-vacuum fractional condensation. Melting ranges: 36.5-36.7° for 1-BrB₅H₈; for 2-BrB₅H₈, -56.0 to -55.7°.

Table I. Volatility of Liquid 1-BrB₅H₈

$$(\log \underline{P} = 5.0374 + 1.75 \log \underline{T} - 0.0033\underline{T} - 2420/\underline{T})$$

$$(t_{760} = 183.1^{\circ}; \text{ Trouton constant} = 20.9 \text{ e.u.})$$

Temp., °C.	36.5	45.9	50.8	56.0	61.8	70.0
<u>P</u> obsd, mm.	3.63	6.03	7.80	10.12	13.31	19.50
<u>P</u> calcd, mm.	3.63	6.05	7.79	10.11	13.37	19.50

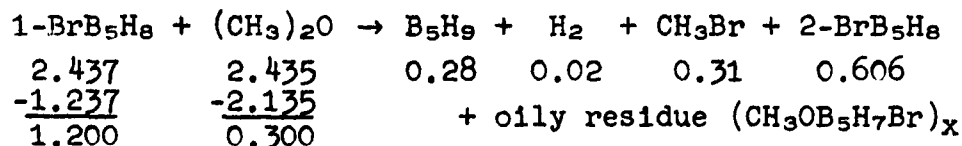
Table II. Volatility of Liquid 2-BrB₅H₈

$$(\log \underline{P} = 5.8959 + 1.75 \log \underline{T} - 0.0045\underline{T} - 2367/\underline{T})$$

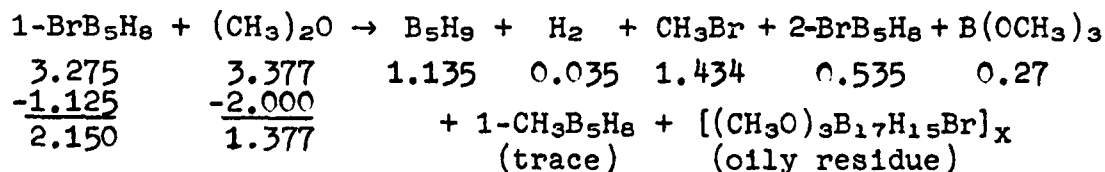
$$(t_{760} = 139.6^{\circ}; \text{ Trouton constant} = 21.16 \text{ e.u.})$$

Temp., °C.	17.80	30.85	34.45	38.50	52.75	59.60
<u>P</u> obsd, mm.	5.82	12.20	14.80	18.35	36.9	50.0
<u>P</u> calcd, mm.	5.80	12.24	14.82	18.31	36.7	50.0

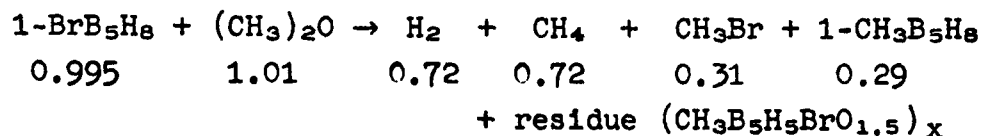
The Dimethyl Ether Reactions. A reaction occurring during 3 days at 0° can be summarized as follows, with stoichiometry in mmoles.



However, a 48-hr. run at 24° gave different results:



Then a 30-hr. process at 38° destroyed all BrB₅H₈ but gave a fair yield of 1-CH₃B₅H₈ (characteristic infrared peaks, 1225, 1229, and 1232 cm⁻¹; no appearance of 2-CH₃B₅H₈ peaks at 1106, 1111, and 1154 cm⁻¹); stoichiometry:



Comparison of the latter two experiments suggests that B(OCH₃)₃ served as a methylating agent. One may speculate whether the unknown CH₃OB₅H₈ was an unstable intermediate.

Methylpentaboranes. The (CH₃)₂O reactions yielded 1-CH₃B₅H₈ but no 2-CH₃B₅H₈; apparently catalysts were lacking. The isomerization is irreversible, as shown by full recovery of 2-CH₃B₅H₈ which had remained with 2,6-(CH₃)₂C₅H₃N for 5 days at 27°— conditions causing complete conversion of 1-CH₃B₅H₈.⁴ This isomerization, when catalyzed in the vapor

(4) T. P. Onak, J. Am. Chem. Soc., 83, 2584 (1961)

phase by $(\text{CH}_3)_2\text{NB}_2\text{H}_5$, does not depend upon transfer of BH_3 groups, for only 4% of a sample of 1- $\text{CH}_3\text{B}_5\text{H}_8$ isomerized during a one-boron $\text{B}^{10}\text{-B}^{11}$ exchange with $(\text{CH}_3)_2\text{NB}_2\text{H}_5$ at 100° . This and other boron isotopic exchanges will be described more fully elsewhere.

For the volatility of 2- $\text{CH}_3\text{B}_5\text{H}_8$ (m.p. -55°), $\log P = 6.889 + 1.75 \log T - 0.0065T - 2212/T$ (accuracy like Table II; example, 19.0 mm. at 0°); thus it is roughly half as volatile as 1- $\text{CH}_3\text{B}_5\text{H}_8$ (34 mm. at 0°).⁵

(5) G. E. Ryschkewitsch et al., Inorg. Chem., 2, 891 (1963)

Infrared Spectra. The infrared peaks shown in Table III were recorded accurately by the Beckman IR7 instrument. After each frequency (cm^{-1}) the relative intensity $k = (100/P)\log I_0/I$ (path 10 cm.; pressure P in mm. at 25°) is given in parentheses. Assignments are omitted because they would be either obvious or controversial.

(Insert
Table III
p. 5)

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Table III
Infrared Spectra of Pentaborane Derivatives

1-BrB ₅ H ₈	2-BrB ₅ H ₈	1-CH ₃ B ₅ H ₈	2-CH ₃ B ₅ H ₈
.	2975(0.54)	2975(1.5)
.	2940(0.65)
.	2931(2.5)	2930(0.86)
.	2862(1.3)	2861(0.32)
2622(7.6)	2622(7.2)	2600(19)	2600(19)
2480(0.36)	2500(0.41)	2440(0.12)
.	1996(0.13)	1940(0.27)
1850(1.8)	1800(0.58)	1840(2.0)	1855(0.93)
1804(0.89)	1718(0.24)	1790(1.3)	1811(0.97)
1625R(0.91)	1625R(0.46)
1602Q(1.10)	1603Q(0.87)	1629(0.34)	1600(0.17)
1585P(0.56)	1584P(0.43)
1442(2.3)	1393(5.5)	1418(2.9)	1435(4.4)
1386(1.6)	1342(0.81)	1386(2.9)	1386(4.9)
.	1330R(0.82)	1330R(1.5)
.	1321Q(1.30)	1315Q(1.6)
.	1314P(0.46)	1310P(1.3)
.	1262(0.32)
.	1232Q(2.1)	1154(1.4)
.	1229(1.9)
1198(1.17)	1225(1.8)	1111(0.65)
1152(2.5)	1120(0.93)	1168(0.20)	1106(0.68)
1065(0.82)	1029	1044R(0.28)	1036
1060(0.90)	1025(3.8)	1036Q(0.52)	1031(0.74)
1055(0.96)	1020	1026P(0.28)	1026
908(2.2)	887	907(5.9)	985(0.17)
861(1.1)	883(3.5)	890(4.3)
. . . .	879
. . . .	856(1.55)	802(0.70)
.	797(0.76)
.	791(0.70)
764	764
762(1.64)	762(0.63)
755	760
648(2.8)	639(2.9)	643(5.1)	643(2.8)

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